Carbonization mechanism of bamboo (*phyllostachys*) by means of Fourier Transform Infrared and elemental analysis

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Abstract: Bamboo was carbonized at different temperatures ranging from 200℃ to 600℃.The dependence of the change of hemicellulose, cellulose, and lignin on the temperature was investigated by means of elemental analysis and Fourier Transform Infrared (FTIR) spectra of the residual solid products. The results showed (1) selow 200℃, hemicellulose in bamboo was decomposed and a large amount of hydroxyl groups are dislocated from hemicellulose and cellulose, accompanied by the evolution of water to escape. (2) 200℃~250℃, cellulose in bamboo was drastically decomposed whereas the net structure of lignin keep stable, with the except of the dislocation of methoxyl groups from lignin. (3) 250℃~400℃, the net structure of lignin collapse, up to 400℃, followed by that the more position in aryl groups are substituted. (4) For bamboo carbonization, the aromatization of residual carbon has approximately completed at the temperature as high as 600℃. But the fusion of aromatic rings possibly does not occur.

Keywords: Bamboo; Carbonization; Fourier Transform infrared; Elemental analysis

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Introduction

Bamboo charcoal, produced from bamboo by use of carbonization technique, has received considerable attention due to with many functions (Park-sangbum 1998) as adsorption, electric magnetic shield, and radiation of infrared ray for recent years. It has been applied in many fields, such as the purification of air, sewage disposal, and health products for people daily life. Carbonization of bamboo, like other lingocellulosic biomass, is a very complex process. The carbonization at lower temperature involves the decomposition of polymer components, evolution of volatile matters, followed by the development of thermally stable aromatic layers and their rearrangement and finally the formation of carbon structures. Therefore, understanding the mechanism of carbonization of bamboo is important to clarify the rules of the main elements of carbon, hydrogen and oxygen, as well as the reactivity of various groups composed of these atoms.

In the organic molecules, a lot of functional groups can absorb radiation in the infrared (IR) region. So, IR spectroscopy has already been applied widely to the carbonization process of biomass, and a large amount of useful information has been obtained. (Yu *et al.* 1989; Morterra and Low 1983, 1984, 1985; Low *et al.* 1985; Roger 1984)

However, the fact that a material absorbs radiation strongly in one spectral region does not require it to absorb strongly, or absorb at all, in another region (Low and Morterra 1983). Consequently, although most solid products of carbonization are black in the visible, i.e. absorb radiation so strongly that the thinnest practical layers are opaque, it may be possible that such a black material has some transparency in the IR region. Then, the transparency can be increased by decreasing the thickness of the layer, so that IR transmission/absorption (T/A) spectroscopy becomes feasible. Excellent results have been obtained in some cases and the sensitivity of T/A measurements has been greatly enhanced by using Fourier Transform (FT) spectroscopy. In the main, however, T/A measurements have proved to be useful only with materials such as coals and chars, i.e materials which have not been strongly heated.

Kmetko (E.A. Kmetko 1951) showed that molecular solids having condensed aromatic structures are semiconductors whose energy gap decreases with the increase of molecular size. When a molecular crystal is heated to progressively higher temperature, decomposition occurs and aromatic domains develop and grow; short-range order increases and the energy gap decreases progressively. After heating at relatively low temperatures, partially decomposed organic materials visually appear black, i.e. there is a complete band of absorption through the visible region, terminating in the near-IR. The results suggested that the narrowing energy gap results in extensive IR absorption for the chars or raw cokes formed in the 500 -700°C.

It is apparent that T/A measurements can be made with

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materials that have not been subjected to high temperatures; they are partially transmitting if made thin enough. This is usually accomplished by fine grinding of samples and using the pelletting techniques. For the black products of bamboo carbonization, T/A measurements are feasible in the qualitative analysis but not in the quantitative one.

The present study deals with the qualitative variety of functional groups in bamboo by using Fourier Transform Infrared (FTIR) technique, and is intended to understand the carbonization mechanism of bamboo.

Materials and methods

Preparation of samples

Bamboo was carbonized in a kiln at temperatures of 200, 250, 300, 350, 400, 500, and 600°C respectively, and with the residence time of 3 hours.

Measurement of infrared spectroscopy

Direct transmission IR spectroscopic studies of the resultant solid products from carbonization of bamboo were performed by using a NICONET IR Spectrophotometer Model 365. The KBr tablets were prepared in the following manner: 1 mg of samples was ground before adding 500 mg of KBr, then the mixture was reground, followed by pelleting 200 mg of the mixture. Spectra were recorded with 100 scans at 2-cm^{-1} resolution.

Elemental analysis

From the aspect of element constitutes, bamboo and bamboo charcoals at the various carbonization temperatures are mainly composed of carbon, oxygen, and hydrogen, besides a small amount of ash such as Si, Mg, Na, Ca, and their oxides. Their contents of carbon (C%, weight basis) and hydrogen (H%, weight basis) were performed in elemental analysis instrument of CHN-O-RAPID (made in Germany) for bamboo and solid products of bamboo carbonization. Analysis was operated with the oven temperature of 1 000°C and burning time of 3 min. The content of ash (A%, weight basis) was measured by means of GB/T 12496.11-90. The content of oxygen (O%, weight basis) was calculated by the equation, O%=100-C%-H%-A%.

Results and discussions

Elemental analysis

The contents of carbon (C%), oxygen (O%) and hydrogen (H%) in bamboo at the various carbonization temperatures are listed in Table 1. Carbon in bamboo and bamboo charcoals exists in the aromatic structures (including those in lignin), namely fixed carbon, and aliphatic chains. The content of the latter carbon, which has still been uncarbonized, can be obtained from that of carbon subtracted by that of fixed carbon in bamboo charcoals.

Table 1. The contents of carbon (C%), oxygen (O%), and hydrogen (H%) of bamboo at the different carbonization temperature

Element	Temperature /°C							
	105	200	250	300	350	400	500	600
C %	46.8	52.1	61.4	70.6	74.9	79.0	82.9	83.7
O%	45.6	40.7	30.8	22.1	18.1	14.2	10.8	10.4
H %	6 6	5.9	5.8	5.1	4.7	4.2	3.6	3.1
Fixed carbon, %	\	22.4	37.5	58.0	66.4	72.6	81.5	83.0
Carbon in aliphatic chains, %	\	29.7	23.9	12.6	8.5	6.4	1.4	0.7

Note: 1. "\" denotes the measurement was not performed.

2. Fixed carbon at carbonization temperatures of 105℃, 200℃, 250℃, 300℃ is mainly related to those of aromatic rings in lignin.

Up to the carbonization temperature of 600°C, Table 1 reveals that the carbonization of bamboo was basically completed and the aromatic structure is dominant in bamboo charcoal. During the carbonization of bamboo, though the weight loss of oxygen is higher than that of hydrogen, the number loss of oxygen atom was lower than that of hydrogen atom. In order to compare the number change of the every kind of atoms, the number loss of carbon, oxygen, and hydrogen atom (mol/g) was calculated during the two-adjacent carbonization temperature, for instance, 105-200°C, 200-250°C, by means of the equation:

$$A=[B_1-(Y_2/Y_1)\times B_2]/M$$

where A is the number loss of carbon, oxygen, and hydrogen atom, mol/g; B_1, B_2 is the content of carbon, oxygen, and hydrogen in bamboo and bamboo charcoals at former and the latter in the every scope of carbonization temperature, respectively; Y_1, Y_2 is the yield of bamboo from the carbonization at former and the latter in the every scope of carbonization temperature, respectively; M is atom weight.

Fig.1 suggests that, from the point of the change of functional groups, the process of carbonization of bamboo can be divided into four stages. (1) below 200°C. Mainly, hydroxyl groups in hemicellulose and cellulose are destructed by heating, which is consistent with the more number loss of hydrogen and oxygen atoms with the very less number loss of carbon atoms and the large amount of water produced in this stage. (2) 200-300°C. The destruction of hydroxyl groups and carbon–oxygen bonds in cellulose and hemicellulose can explain the losses of a large number of hydrogen, oxygen, and carbon atoms. (3) 300-500°C. There are a more number of carbon-hydrogen bonds and carbon-carbon bonds destroyed by heating relating to the

other bonds involved in the decomposition of lignin. It can be deduced from the fact that the loss of the number of hydrogen atoms is still more, by comparison with that of hydrogen and oxygen atoms. (4) Above 500°C. In this period, a lot of carbon-hydrogen bonds and carbon-carbon bonds are destructed in bamboo charcoal, as associated with the aromaticity of carbon atoms, which is suggested by the loss of the number of carbon atoms increases with the elevation of carbonization temperature.

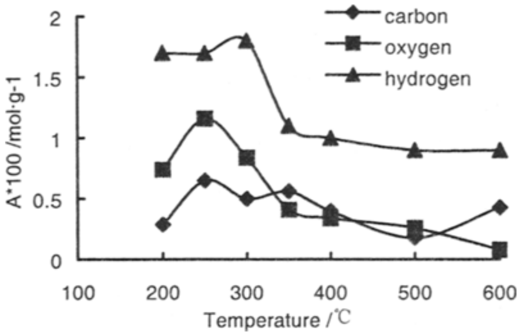

Fig. 1 The number loss of carbon, oxygen, and hydrogen atom, as a function of carbonization temperature

FTIR analysis

FTIR spectrum of bamboo

For bamboo the FTIR spectroscopy (Fig.2) provides information on the chemical structure of the material. Band assignments (Zhang *et al.* 1993; Politou *et al.* 1990; Roger *et al.* 1964; Vicente Gómez-Serrano *et.al.*1999) for the spectrum of bamboo which were summarized in Table 2, indicate that bamboo contains a number of atomic groups and structures (OH, CH_2, C=O, C-O-C, and so on). The position and shape of the band at 3 420 $cm^{-1}$are compatible with the involvement of the hydroxyl groups in hydrogen bonding. Otherwise, the band should be located at significantly higher wavenumbers and much sharper. According to the four types of hydrogen-bonded structures reported previously by Painter, *et al.*, the predominant one in bamboo is self-associated OH groups as in this case the band is centered at 3 400 cm^{-1}. The fact that, in the spectrum of bamboo, the band at 3 420 cm^{-1} was slightly broader than lower wavenumber suggests that bamboo also contains OH-ether hydrogen bonds, which absorb infrared radiation at 3 300 cm^{-1}. Other spectral bands connected with the OH groups, which appeared at lower wavenumbers than 3 420 cm^{-1}, were those caused by δ (O-H),.υ (C-O), and γ (O-H) absorptions. The δ (O-H) band is only of complementary significance in identification studies and the υ (C-O) band occurs in the same spectral region as other absorptions. The great intensity of the band at 1 047 cm^{-1} denotes the presence on bamboo of a high concentration of primary hydroxyl groups. The γ (O-H) band has not practical value. The spectrum bands as mentioned above are mainly related to the structure of hemicellulose and cellulose in bamboo, in addition to the bands at 1 110 cm^{-1} ,1 160 cm^{-1}, and 980 cm^{-1}, considering the fact that the FTIR spectroscopy of cellulose has the strongest and characteristic spectrum bands (Chen 1988) at 1 058 cm^{-1} with shoulder bands at 1 162 cm^{-1}, 1 122 cm^{-1}, and 985 cm^{-1}, which originate from the absorptions of υ (C-O) and δ (O-H).

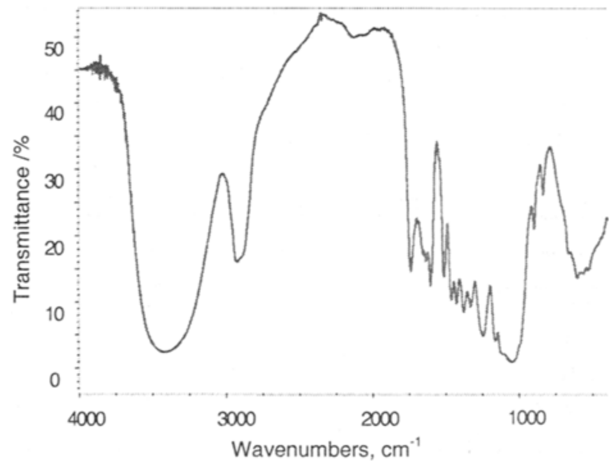

Fig. 2 FTIR spectrum of bamboo

Table 2. FTIR spectrum for bamboo

Band position, cm^{-1}	Assignment *	Band position, cm^{-1}	Assignment *
3420	υ (O-H)	1244	υ$_{as}$(=C-O-C)
2923	υ (C-H)	1160	υ$_{as}$(C-O-C)
1735	υ (C=O)	1110	υ (C-O)
1604, 1508, 1460	υ (C=C)	1047	υ (C-O), δ (O-H)
1460	δ$_{as}$(CH_3,CH_2 scissor)	897	δ (C-H), γ (O-H), γ (C-H)
1424	δ (O-H)	834	γ (C-H)
1375	δ$_s$(CH_3)	604	γ (O-H)
1329	δ (O-H), υ (C=O)		

* υ , stretching; δ , bending (in-plane); γ , bending (out-of-plane); s, symmetric; as, asymmetric.

Since the band at 2 923 cm^{-1} is broad and displays shoulders, it must represent υ$_{as}$ and υ$_s$ vibration modes of methyl and methylene groups. The characteristic absorption of the methyl group near 1 375 cm^{-1} is diagnostically

useful. Also, the region near 1 400 cm^{-1} gives some idea of the relative abundance of CH_2 and CH_3 groups. In general, for organic compounds, the intensity of the band at 1 460 cm^{-1} is frequently stronger than that of the band at 1 375 cm^{-1}. Reverse intensity relationships would be in accordance with the presence of acetoxy groups in a given compound. In the spectrum of bamboo, as can be noted, the band at 1 375 cm^{-1} is somewhat more intense than the band at 1 460 cm^{-1}. Other bending vibrational modes for the CH_2 groups (i.e. rocking, wagging and twisting) give rise to spectral bands at lower wavenumbers. These bands are usually weak and of little practical utility.

In the range from around 1 600 cm^{-1} to 1 450 cm^{-1}, the bands at 1 604 cm^{-1}, 1 508 cm^{-1}, and 1 460 cm^{-1} are attributable to skeleton stretching vibration of aromatic rings, which are mainly concerned with lignin in bamboo. For these systems, the 1 460 cm^{-1} peak overlaps with υ_{as} vibrational modes of CH_2 and CH_3 groups. The single band at 834 cm^{-1} is compatible with γ (C-H) vibrations in aromatic ring systems having two- adjacent- hydrogen atoms, as can be explained by the higher content of p-Coumaryl alcohol and coniferyl alcohol among lignin precursors. However, since γ (C-H) vibrations in aromatic ring systems having one hydrogen atoms are usually weak and possibly overlap with δ (C-H), γ (O-H) of vibrational modes, it is uncertain that the band at 897 cm^{-1} is associated with γ (C-H) vibrations in aromatic ring systems having one hydrogen atoms. Moreover, the band at 1 244 cm^{-1} corresponds to υ_{as} (=C-O-C) of vibrational mode, which possibly originates from lignin.

The high intensity of the band at 1 735 cm^{-1} points out there has a lot of carbonyl groups in bamboo. Such a band position indicates the C=O groups are not involved in conjugation with a double bond or aryl group in bamboo. Otherwise, the band should shift significantly to lower wavernumbers. This is in line with the absence of the band at around 1 580 cm^{-1} in the aromatic skeletal stretching vibration, which appears when phenyl groups are conjugated with unsaturated groups or groups having lone pair electrons.

Carbonization of bamboo

As shown in Fig. 3, the change of the functional groups in the bamboo products due to carbonization depends upon the temperature.

1) below 200°C: Compared with the FTIR spectrum of bamboo, for that of the product from bamboo charred at 200°C, the bands at 3 420 cm^{-1} and 1 047 cm^{-1} become sharper and the band at 1 110 cm^{-1} becomes single, the intensity of the band at 2 923 cm^{-1} decreases. These facts suggest that a large number of hydroxyl bonds are lost in bamboo by heating at such temperatures. Also, hemicellulose in bamboo is partly decomposed into fractions, part of which escape from bamboo.

2) 200-250°C: At the temperature ranging from 200°C to 250°C, the structure of cellulose in molecule level was fully destructed and methoxyl groups in lignin were dislocated. The fact that the intensity of the characteristic bands at 1 160-980 cm^{-1} of cellulose in bamboo get very weak, together with the disappearance of the band at 1 329 cm^{-1}, indicates that the decomposition of cellulose in bamboo is almost complete in this scope of temperature. Moreover, the drastic decrease of the band (Xie 1987) at 897 cm^{-1} is compatible with the complete destruction of pyranoid rings in cellulose. At the same time, it is noted that the band at 1 375 cm^{-1} disappears, which reveals that methyl groups in bamboo are almost lost by heating and is consistent with the reduction of the intensity of the band near 2 924 cm^{-1}. These methyl groups possibly come from the dislocation of methoxyl groups connected with aryl groups in lignin, which is also supported by the decrease of the intensity of the band at 1 244 cm^{-1} , i.e. υ_{as}(=C-O-C) and the slight increase of the intensity of the band at 834 cm^{-1}. But the bands from 1 600-1 450 cm^{-1}, which are related to aromatic nuclei in lignin, keep stable. Therefore, it can be inferred that the basic net structure in lignin is not destructed.

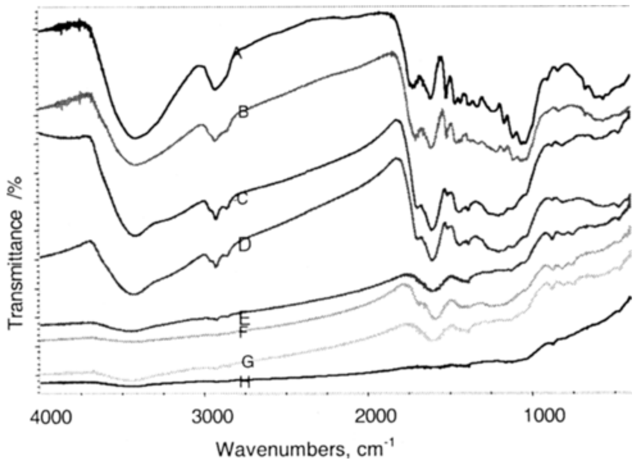

Fig. 3 FTIR spectra of the products carbonized at various temperatures.
A, B, C, D, E, F, G, and H correspond to represent the carbonization temperatures of 200°C, 250°C, 300°C, 350°C, 400°C, 500°C, and 600°C, respectively. The value of the ordinate is eliminated to compare the various spectra

3) 250-400°C: FTIR spectra of the products carbonized at 250°C-400°C shows four main features. (A) The decomposition of lignin. It is significant that the band at 1 510 cm^{-1}, as (Vicente Gómez-Serrano *et al.* 1999) indicative of 1,4- and /or 1,2,4 substitutions in aromatic rings, decreases in intensity and disappears up to 400°C, which is accompanied by the shift of the band position at 834 cm^{-1} toward the lower wavenumbers. (B) The aromatization of carbon atoms. Starting from the carbonization temperature of 300°C, the trio of bands of the wagging vibration mode of the aromatic CH groups at 870 cm^{-1}, 810 cm^{-1} and 750 cm^{-1} appear and become a trio of well-resolved bands at 400°C, as indicative of the first appearance of an aromatic network. However, the aromatic C-H band of stretching vibration mode near 3 100 cm^{-1} is possible to be so weak that it is not

readily detectable, but accompanying wagging bands are readily observable. (C) The C=O bonds decrease in amount and become conjugated with the aromatic rings. In the FTIR spectrum, it is supported by the intensity of the band at 1 735 cm^{-1} declines remarkably and the band at 1 604 cm^{-1} shifts to somewhat lower wavenumbers with the increase of the intensity. Though the assignment of the band near 1600 cm^{-1} observed in most of carbonaceous materials has been controversial for decades years (Akhter *et al.* 1985), it is generally accepted that the intensification of the band is due to the C=O group conjugated with an aromatic system being responsible for the low absorption wavenumbers of C=O groups. (D) Up to 400°C, the band of hydroxyl group of stretching modes approximately disappears. Therefore, the product carbonized at the temperature as high as 400℃ does not posses hydroxyl groups.

4) 400-600°C: FTIR spectrum of the product carbonized at carbonization temperature as high as 600°C becomes nearly flat. Nevertheless, apparently, that the band at 870 cm^{-1} becomes stronger whereas the bands at 810 cm^{-1} and 780 cm^{-1} become weaker with the elevation of carbonization temperature. This is in line with the presence in the carbonized of a higher concentration of aromatic rings with a large degree of substitution. Also, the stretching band of C=O groups disappears and the band near 1 600 cm^{-1} becomes broader attributed to the conjugation of C=O bond with the aromatic rings. In addition, the stretching band of CH groups basically disappears. These changes coincide with the full aromatization of carbon in bamboo charcoal. But it should be pointed out that bamboo charcoal obtained at carbonization temperature of 600°C possibly contains the small amount of the aliphatic bridges, carbon atoms of which are mainly linked with aryl groups. However, the decrease of the intensity of the band near 1 600 cm^{-1} is possibly related to the lower content of oxygen, which is to be investigated further.

Conclusions

Combined with the elemental analysis, FTIR spectra of the bamboo products carbonized at various temperatures can be applied to determinate the decomposition temperature of hemicellulose, cellulose and lignin in bamboo. The following conclusion can be drawn:

Below 200°C, hemicellulose in bamboo is decomposed and a large amount of hydroxyl groups are dislocated from hemicellulose and cellulose, and then produce water to escape.

200-250°C, with regard to the significant decrease of the intensity of the strong and characteristic bands at 1 160-980 cm^{-1} and the band of δ(C-H) near 897 cm^{-1} in cellulose , cellulose in bamboo is drastically decomposed, including pyranoid rings, whereas the net structure of lignin keeps stable, with the except of the dislocation of methoxyl groups from lignin, mainly according to the disappearance of the band of $\delta_s(CH_3)$.

250-400°C, the net structure of lignin completely collapses, followed by that the more positions in aryl groups are substituted, based on the disappearance of the band at 1 510 cm^{-1}, which originates in the skeletal vibration, as well as the change of the relative intensity of a trio-bands at 780 cm^{-1}, 810 cm^{-1}, and 780 cm^{-1},

For bamboo carbonization, considering that the content of carbon in aliphatic chains is very low, the aromatization of residual carbon has approximately completed at the temperature as high as 600°C.But the fusion of aromatic rings possibly does not occur.

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